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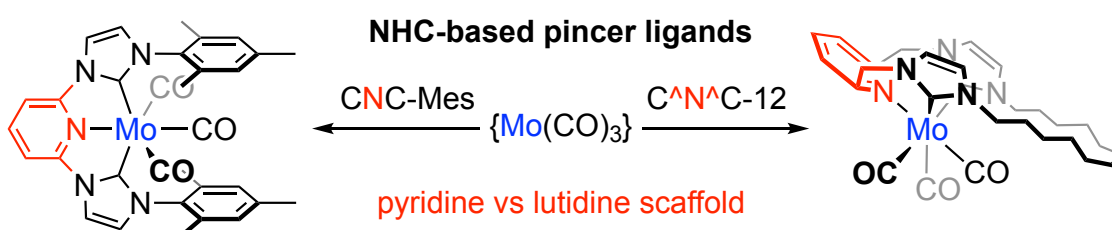
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Divergent stereoisomers of molybdenum carbonyl complexes of NHC-based pincer ligands

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TOC graphic:



Keywords: Molybdenum, NHC, pincer ligands, coordination geometry

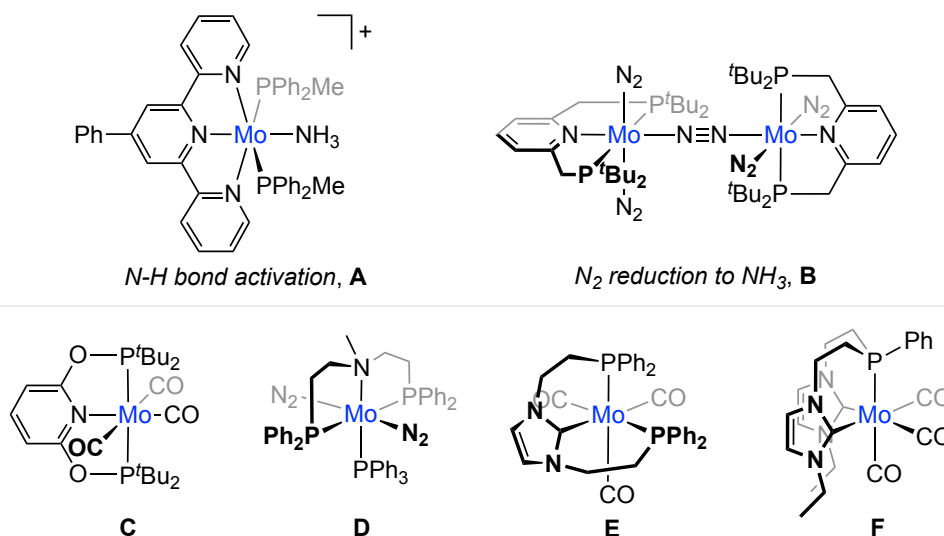
Abstract

The first molybdenum complexes of widely used NHC-based CNC and C[^]N[^]C pincer ligands are described, viz. [Mo(L)(CO)₃] (L = 2,6-bis(mesityl-imidazolylidene)pyridine \equiv CNC-Mes, **1**; α,α' -(diimidazolylidene-dodecamethylene)lutidine \equiv C[^]N[^]C-12, **2**). These complexes have been thoroughly characterised in solution and the solid-state, revealing different stereochemical preferences of the tridentate ligands depending on the nature of the scaffold. In the case of flexible C[^]N[^]C-12 an uncommon *fac*-coordination geometry is observed, whilst the complex of rigid CNC-Mes adopts the expected *mer*-configuration. For the combination of donors associated with the ligands, DFT calculations establish preferential *fac*-coordination, however, within the CNC ($\Delta\Delta G = +63.1 \text{ kJ}\cdot\text{mol}^{-1}$) and C[^]N[^]C ($\Delta\Delta G = +20.0 \text{ kJ}\cdot\text{mol}^{-1}$) scaffolds this conformation is significantly destabilised relative to the *mer*-alternative.

Introduction

Fueled by flourishing applications in catalysis and materials science, pincer ligands featuring *N*-heterocyclic carbene (NHC) donors are becoming increasingly prominent in contemporary organometallic chemistry.^{1,2} These ligands combine the strong σ -donor characteristics of NHCs with the favorable thermal stability and reaction control possible with a tridentate geometry. While the structural diversity of this ligand class continues to evolve, prototypical variants bearing two imidazolylidene donors connected by pyridyl (CNC) and lutidyl (C[^]N[^]C) coordinating backbones remain the most heavily investigated.^{1,3} The former are characterised by rigid structures and adoption of obtuse C–M–C bite angles on coordination, while the presence of methylene spaces in the latter confers flexibility and enables binding of metals with more linear C–M–C bite angles. In addition to divergent electronic and steric characteristics, the flexible nature of the C[^]N[^]C scaffold is also manifested in the ability of these ligands to deviate from the expected *mer*-tridentate geometry; well-defined examples, however, are rare and limited to a series of Ru(II) complexes of the formulation *fac*-[Ru(C[^]N[^]C)(PPh₃)(CO)(H)]⁺.⁴

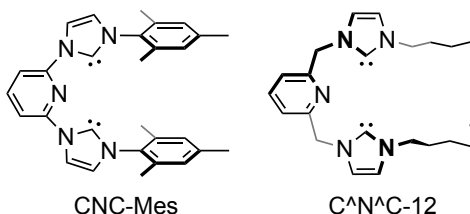
Chart 1. Molybdenum complexes of tridentate ligands.



Stimulated by recent breakthroughs in molybdenum chemistry exploiting pincer ligands, such as the coordination induced activation of N-H bonds (**A**)⁵ or catalytic reduction of N₂ to NH₃ (**B**),^{6,7} and building on related examples (e.g. **C** – **F**, Chart 1),^{8,9,10,11} we became interested in developing the organometallic chemistry of molybdenum adducts of CNC and C[^]N[^]C ligands. We herein describe the preparation and characterisation of the *first* molybdenum complexes of NHC-based pincer ligands of these types, from coordination of {Mo(CO)₃} fragments to archetypical CNC-Mes

and macrocyclic C[^]N[^]C-12 (Chart 2). Late transition metal complexes of the latter have been investigated in our laboratories over the last few years.^{12,13,14}

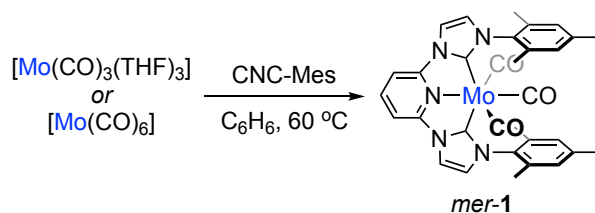
Chart 2. NHC-based pincer ligands CNC-Mes and C[^]N[^]C-12



Results and discussion

Bulky and conformationally rigid CNC-Mes was prepared and subsequently isolated in the solid-state using an established literature protocol,¹⁵ involving deprotonation of the corresponding pro-ligand CNC-Mes·2HBr.¹⁶ Following initial *in situ* experiments, indicating quantitative complexation by ¹H NMR spectroscopy, Mo(0) complex *mer*-[Mo(CNC-Mes)(CO)₃] (*mer*-1) was prepared by direct reaction between the singlet carbene CNC-Mes and [Mo(CO)₆] in benzene at 60 °C and subsequently isolated in moderate yield on crystallisation at RT (29%, Scheme 1). The complex can also be prepared in essentially equivalent yield (26%) when employing [Mo(CO)₃(THF)₃] as the metal precursor.

Scheme 1. Synthesis of molybdenum complex *mer*-1



The structure of *mer*-1 was confirmed through a combination of solution (CD₂Cl₂ / CH₂Cl₂) and solid-state methods. Coordination of CNC-Mes is verified by presence of a characteristic high frequency carbenic resonance (δ 220.6),¹⁷ alongside two distinct carbonyl signals at δ 244.2 and 210.1 in approximate 1:2 ratio, in the ¹³C{¹H} NMR spectrum – assignments verified by an HMBC experiment. Assuming hindered rotation of the mesityl wingtip, alternative formulation as the *fac*-isomer (*C_s* symmetry) in solution can be discounted on the basis of the NMR data that indicates *C_{2v}* symmetry. For instance, only two methyl resonances are observed (in a 1:2 ratio) in both the ¹H and ¹³C{¹H} NMR spectra; three in a 1:1:1 ratio are expected for *C_s* symmetry. Three carbonyl bands are observed in the IR spectrum (1921, 1829, 1807 cm⁻¹) substantiating the connectivity, but

not discriminating between *mer*- or *fac*-binding of CNC-Mes. It is instead only from the solid-state structure of *mer*-**1** that definitive corroboration of the, albeit expected, *mer*-coordination geometry can be made (Figure 1). Presumably as a consequence of subtle crystal packing effects, the X-ray derived structure of *mer*-**1** is distorted away from the overall C_{2v} symmetry observed in solution to crystallographically enforced C_2 symmetry (*Fdd2* space group), with the molybdenum centre adopting a significantly distorted octahedral geometry (C18-Mo1-C18*, 146.2(5) °; C4-Mo1-C4*, 162.7(4) °; N10-Mo1-C2, 180 °). A similar geometry has been reported for PONOP-ligated **C** (P-Mo-P, 150.02(2) °; OC-Mo-CO, 162.97(6) °; N-Mo-CO, 175.79(5) °), and the bonding metrics are in close agreement (e.g. Mo1-C2: 1.97(2) Å, *mer*-**1**; 1.966(2) Å, **C**; Mo1-C4: 2.021(8) Å, *mer*-**1**; 2.010(2)/2.024(2) Å, **C**).⁸

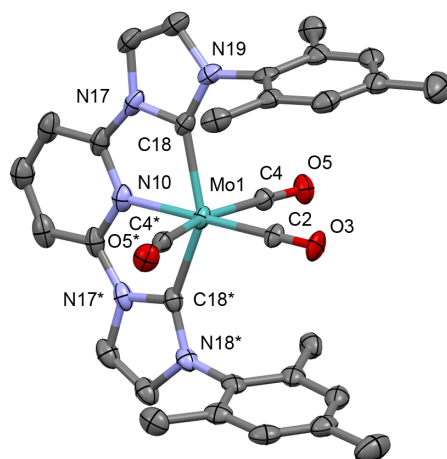
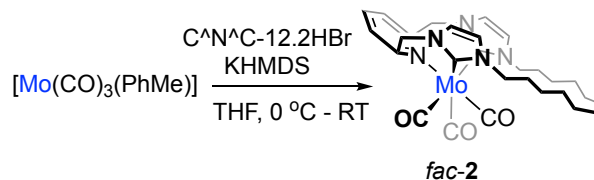


Figure 1. Solid-state structure of *mer*-**1**. Thermal ellipsoids drawn at the 30% probability level; solvent molecule and hydrogen atoms omitted for clarity. The starred atoms are generated by the symmetry operation 1-x,1-y,z. Selected bond lengths (Å) and angles (deg): Mo1-C2, 1.97(2); Mo1-C4, 2.021(8); Mo1-N10, 2.17(2); Mo1-C18, 2.146(8); N10-Mo1-C2, 180; C4-Mo1-C4*, 162.7(4); C18-Mo1-C18*, 146.2(5).

Coordination of C^NC-12 to group 9 and 10 metals has previously been realised through transmetallation reactions of coinage-metal derivatives of C^NC-12·2HBr.¹⁴ Following unsatisfactory results employing reactions of a silver transfer agent, generated from reaction between Ag₂O and C^NC-12·2HBr in the presence of a halide abstractor, we reverted to a strategy analogous to that used for *mer*-**1**. Recognising the significantly lower stability of the free carbene it was instead generated *in situ*, through deprotonation by a stoichiometric quantity of strong base, directly in the presence of a metal precursor. Preliminary NMR-scale experiments involving heating with [Mo(CO)₆] in C₆D₆ indicated formation of *fac*-[Mo(C^NC-12)(CO)₃] (*fac*-**2**; *vide infra*), but in low yield. Reflecting the stereochemistry of the complex and need for more mild

conditions, a preparative procedure involving low temperature deprotonation of C[^]N[^]C-12·2HBr in the presence of [Mo(CO)₃(PhMe)] was developed (THF, 0 °C; Scheme 2) enabling analytically pure *fac*-**2** to be isolated in a practicably useful yield (54 %).

Scheme 2. Synthesis of molybdenum complex *fac*-**2**



In CD₂Cl₂ solution, the ¹H and ¹³C NMR spectroscopic characteristics of *fac*-**2** are consistent with tridentate coordination of C[^]N[^]C-12 to a central molybdenum carbonyl fragment; evidenced firstly by absence of high frequency imidazolium ¹H signal of the corresponding pro-ligand (δ 10.8),¹² but more conclusively by the presence of three high frequency ¹³C resonances attributed to the coordination of the carbene (δ 201.0) and carbonyl ligands (δ 233.0, 225.3; ~ 1:2 ratio) – assignments verified by an HMBC experiment. These ¹³C data are notably different to those of *mer*-**1**, with the carbenic resonance 20 ppm lower in frequency, while those of the carbonyl are perturbed by approximately 10 ppm. Such differences strongly suggest *fac*-coordination of C[^]N[^]C-12 as this configuration places the NHC donors *trans* to the carbonyl ligands. Indeed ¹³C signals of very similar magnitude are observed for the NHC and *trans*-disposed carbonyl ligands in **F** (δ_{N_CN} 195.5; δ_{C_O} 224.9).¹⁰ The presence of diastereotopic methylene ¹H resonances and presence of three carbonyl stretching bands (1893, 1771, 1771 cm⁻¹, CH₂Cl₂; 1880, 1767, 1736 cm⁻¹, ATR) are also consistent with *fac*-coordination, but as for *mer*-**1** these data in isolation do not definitively discriminate against an alternative formulation as the *mer*-isomer (C₂ vs C_s symmetry). As for the ¹³C data the significantly reduced magnitude of the carbonyl stretching frequencies in comparison to *mer*-**1** is, however, symptomatic of *trans*-coordinated NHC donors.

Ultimately the assignment of **2** to a *fac*-coordination geometry is corroborated by structural determination in the solid-state by X-ray crystallography (Figure 2). Reflecting the flexibility and conformation of the NHC-based pincer ligand, the metal adopts an almost ideal octahedral coordination geometry, with approximately linear N1-Mo1-C2, C18-Mo1-C4, C24-Mo1-C6 bond angles. In comparison to *mer*-**1**, the solid-state structure of *fac*-**2** is notable for shorter Mo-CO bonds (1.924(5) vs. 1.97(2) Å; 1.971(6)/1.972(6) vs. 2.021(8) Å), but elongated Mo1-C18/24 (2.282(5)/2.247(6) vs. 2.146(8) Å) and Mo1-N10 bonds (2.350(5) vs. 2.17(2) Å); presumably reflecting stronger M-CO bonding (*cf.* IR data) and a less constrained geometry, respectively. The

dodecamethylene chain is notable for adopting a conformation reminiscent of square like [3333] conformations of cyclododecane rings.¹⁸

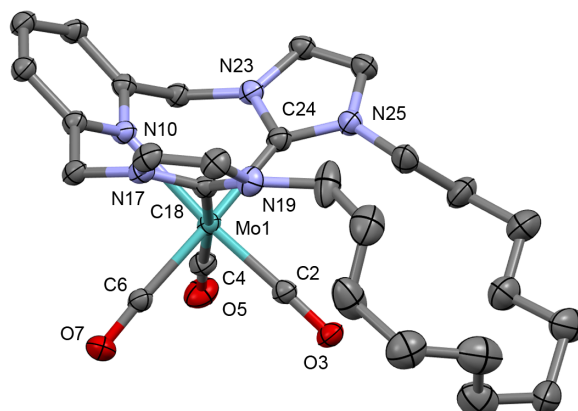


Figure 2. Solid-state structure of *fac*-**2**. Thermal ellipsoids drawn at the 30% probability level; solvent molecules and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1-C2, 1.924(5); Mo1-C4, 1.971(6); Mo1-C6, 1.972(6); Mo1-N10, 2.350(5); Mo1-C18, 2.282(5); Mo1-C24, 2.247(6); N10-Mo1-C2, 174.1(2); C18-Mo1-C4, 173.3(2); C24-Mo1-C6, 167.4(2); C18-Mo1-C24, 100.26(19).

Given the contrasting outcomes associated with coordination of CNC-Mes and C^N^C-12 to {Mo(CO)₃}, we sought to investigate the stereochemical preferences of these systems further. Firstly in attempt to rule out kinetic selectivity, solutions of isolated *mer*-**1** and *fac*-**2** in THF were heated at 60 °C over 48 h. Both complexes, however, proved thermally stable under these conditions, with no significant changes apparent by ¹H NMR spectroscopy, suggesting that they are the thermodynamically most stable isomers. We then turned to quantify the inherent electronic factors behind the contrasting coordination geometries using DFT calculations employing truncated models of **1** and **2** (*i.e.* **1'** and **2'**), alongside a hypothetical system free of geometric constraints imposed by a pincer scaffold, *viz.* [Mo(imidazolylidene)₂(pyridine)(CO)₃] (**3'**): optimised geometries at the ωB97X-D3 level of theory are presented in Figure 3. From the calculated data for **3'** we conclude that a *fac*-coordination geometry is significantly thermodynamically preferred over the *mer*- alternative for the specific combination of donors associated with the CNC and C^N^C ligands ($\Delta G_{\text{fac,mer}} = -20.5 \text{ kJ}\cdot\text{mol}^{-1}$). The geometric constraints associated with the lutidine-based pincer backbone in **2'** partial offset this preference, but the C^N^C ligand remains flexible enough for *fac*-**2'** to be lower in free energy than *mer*-**2'**, albeit marginally ($\Delta G_{\text{fac,mer}} = -0.5 \text{ kJ}\cdot\text{mol}^{-1}$). In the context of the experimental data for *fac*-**2**, which suggests a more substantial preference, the magnitude of this calculated difference for **2'** implies the macrocyclic nature C^N^C-12 plays a role in pre-disposing it towards *fac*-coordination in **2**. In

line with the experimental findings and expectation, *mer-1'* is calculated to be significantly more thermodynamically stable than *fac-1'* ($\Delta G_{\text{fac,mer}} = +42.6 \text{ kJ}\cdot\text{mol}^{-1}$). The CNC scaffold therefore appears to destabilise the *fac*-coordination geometry by $\Delta\Delta G_{\text{fac,mer}} = +63.1 \text{ kJ}\cdot\text{mol}^{-1}$ relative to the *mer*-alternative; three times greater than that of the C^N^C ligand ($\Delta\Delta G_{\text{fac,mer}} = +20.0 \text{ kJ}\cdot\text{mol}^{-1}$).

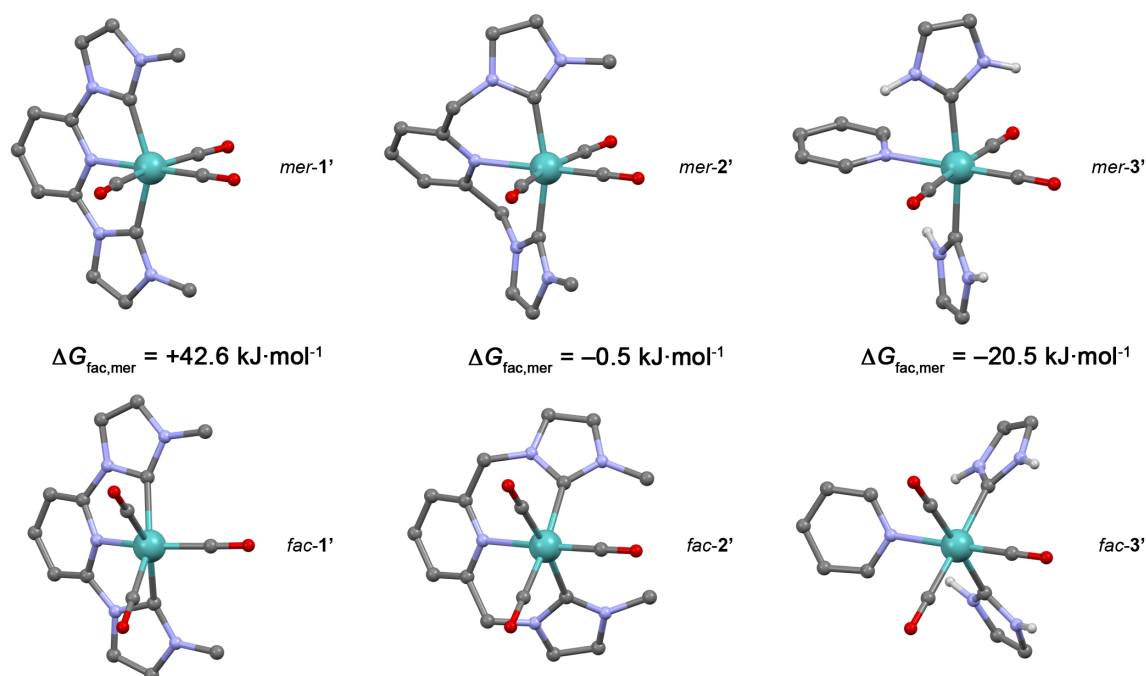


Figure 3. Optimised geometries of isomers of **1'**, **2'**, and **3'** [ω B97X-D3/LANL2DZ (Mo), 6-31G(d,p) (others)] with differences in calculated free energy (*fac* – *mer*). Most hydrogen atoms omitted for clarity.

Summary

The first molybdenum complexes of widely used NHC-based CNC and C^N^C pincer ligands have been prepared, viz. $[\text{Mo}(\text{L})(\text{CO})_3]$ (L = 2,6-bis(mesityl-imidazolyli-dene)pyridine \equiv CNC-Mes, **1**; α,α' -(diimidazolyli-dene-dodecamethylene)lutidine \equiv C^N^C-12, **2**). These complexes have been thoroughly characterised in solution and the solid-state, revealing different stereochemical preferences of the tridentate ligands depending on the nature of the scaffold. In the case of flexible C^N^C-12 an uncommon *fac*-coordination geometry is observed, whilst the complex of rigid CNC-Mes adopts the expected *mer*-configuration. For the combination of donors associated with the ligands DFT calculations establish preferential *fac*-coordination, however, within the CNC ($\Delta\Delta G = +63.1 \text{ kJ}\cdot\text{mol}^{-1}$) and C^N^C ($\Delta\Delta G = +20.0 \text{ kJ}\cdot\text{mol}^{-1}$) scaffolds this conformation is significantly destabilised relative to the *mer*-alternative.

Experimental

General considerations

All manipulations were performed under an inert atmosphere, using Schlenk and glove box techniques unless otherwise stated. Glassware was oven dried and flamed under vacuum prior to use. THF, benzene and C₆D₆ were distilled from Na, freeze-pump-thaw degassed and stored under argon over 3 Å sieves. CD₂Cl₂ was dried over molecular sieves (3 Å) and stored under an argon atmosphere. All other anhydrous solvents (< 0.005% H₂O) were purchased from ACROS or Aldrich and used as supplied. CNC-Mes,^{15,16} C^N^C-12.2HBr,¹² and [Mo(CO)₃(PhMe)]¹⁹ were synthesised according to literature procedures. All other reagents are commercial products and were used as received. NMR spectra were recorded on Bruker spectrometers at 298 K unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer. Microanalyses were performed at Elemental Microanalysis Ltd.

Preparation of *mer*-1

Method A: A stirred solution of CNC-Mes (42 mg, 0.09 mmol) and [Mo(CO)₆] (26 mg, 0.10 mmol) in benzene (3 mL) was heated at 60 °C for 16 hours. The resulting dark brown solution was cooled, concentrated and left to stand at 8 °C to afford the product as dark brown crystals, which were isolated by filtration and washed with pentane. Yield: 17 mg (29%).

Method B: A stirred solution of [Mo(CO)₆] (97 mg, 0.37 mmol) in THF (5 mL) was heated at 40 °C for 30 minutes. The resulting yellow solution was cooled to RT and the solvent removed *in vacuo* to afford crude [Mo(CO)₃(THF)₃]. CNC-Mes (150 mg, 0.34 mmol) was subsequently added and the mixture dissolved in benzene (5 mL), and heated at 60 °C for 16 hours with stirring. The resulting dark brown solution was cooled, concentrated and left to stand at 8 °C to afford the product as dark brown crystals, which were isolated by filtration and washed with cold benzene. Yield: 55 mg (26%).

¹H NMR (500 MHz, CD₂Cl₂): δ 7.83 (t, ³J_{HH} = 8.1, 1H, py), 7.77 (d, ³J_{HH} = 2.1, 2H, imid), 7.21 (d, ³J_{HH} = 8.1, 2H, py), 7.09 (d, ³J_{HH} = 2.1, 2H, imid), 6.95 (s, 4H, Mes), 2.30 (s, 6H, CH₃), 2.07 (s, 12H, CH₃).
¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 244.2 (CO), 220.7 (NCN), 210.1 (CO), 152.7 (py), 138.7 (Mes), 137.3 (Mes), 137.2 (py), 136.1 (Mes), 129.1 (Mes), 125.0 (imid), 115.6 (imid), 103.2 (py), 21.3 (CH₃), 18.2 (CH₃). **Anal.** Calcd for C₃₂H₂₉MoN₅O₃ (627.58 g·mol⁻¹): C, 61.24; H, 4.66; N, 11.16.

Found: C, 60.94; H, 4.84; N, 11.63. IR (CH₂Cl₂): $\nu(\text{CO}) = 1921, 1829, 1807 \text{ cm}^{-1}$. IR (ATR): $\nu(\text{CO}) = 1911, 1823, 1775 \text{ cm}^{-1}$.

Preparation of *fac*-2

To a stirred solution of C[^]N[^]C-12.2HBr (80 mg, 0.14 mmol) and [Mo(CO)₃(PhMe)] (44 mg, 0.16 mmol) in THF (2 mL) cooled to 0 °C was added a solution of KHMDS (60 mg, 0.31 mmol) in THF (1 mL). The resulting orange suspension was stirred for 1 hour and warmed to RT. After stirring for a further 4 hours the suspension was concentrated to dryness and the product extracted with excess CH₂Cl₂. The product as an orange powder was obtained on removal of the solvent *in vacuo*. Yield: 46 mg (56%).

¹H NMR (500 MHz, CD₂Cl₂): δ 7.74 (t, ³J_{HH} = 7.6, 1H, py), 7.42 (d, ³J_{HH} = 7.6, 2H, py), 7.06 (d, ³J_{HH} = 1.8, 2H, imid), 6.92 (d, ³J_{HH} = 1.8, 2H, imid), 5.74 (d, ²J_{HH} = 14.1, 2H, py-CH₂), 5.05 (d, ²J_{HH} = 14.1, 2H, py-CH₂), 4.79 (td, ²J_{HH} = 12.5, ³J_{HH} = 5.0, 2H, N-CH₂), 3.87 (td, ²J_{HH} = 12.5, ³J_{HH} = 4.8, 2H, N-CH₂), 2.04 – 2.15 (m, 2H, CH₂), 1.79 – 1.90 (m, 2H, CH₂), 1.22 – 1.65 (m, 16H, CH₂). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 233.0 (CO), 225.3 (CO), 201.0 (NCN), 158.7 (py), 137.8 (py), 123.8 (py), 122.2 (imid), 119.7 (imid), 57.9 (s, py-CH₂), 52.1 (N-CH₂), 32.1 (CH₂), 27.8 (CH₂), 27.1 (CH₂), 26.6 (CH₂), 25.4 (CH₂). **Anal.** Calcd for C₂₈H₃₅MoN₅O₃.⁵/₄CH₂Cl₂ (691.74 g·mol⁻¹): C, 50.79; H, 5.46; N, 10.12. Found: C, 50.83; H, 5.25; N, 9.99. IR (CH₂Cl₂): $\nu(\text{CO}) = 1893, 1771$ (2 coincident) cm^{-1} . IR (ATR): $\nu(\text{CO}) = 1880, 1767, 1736 \text{ cm}^{-1}$.

Computational details

Density functional theory calculations were carried out using the ORCA 4.0.0.2 programme²⁰ package employing Grimme's dispersion corrected ω B97X-D3 functional,²¹ the LANL2DZ basis set and effective core potential for Mo and 6-31G(d,p) basis set for all other atoms.²² Minima were verified by analytical vibrational mode analysis. A range of different conformations were assessed for each isomer of **3'**: those presented herein were found to be the lowest energy. Thermal corrections (298.15 K, 1 atm) were applied to deduce the Gibbs free energies. Cartesian coordinates of all optimised structures are provided as part of the ESI; the associated energies and calculated carbonyl stretching frequencies are provided in Table 1.

Table 1. Selected properties of optimised structures of isomers of **1**, **2'** and **3'**

Compd.	E / a.u.	G / a.u.	H / a.u.	T×S / a.u.	v(CO) / cm ⁻¹
<i>mer-1'</i>	-1184.2270900	-1183.9957351	-1183.9243736	0.0713615	2091 (A ₁), 2023 (B ₂), 1968 (A ₁)
<i>fac-1'</i>	-1184.2087850	-1183.9795105	-1183.9061570	0.0733535	2078 (A'), 2019 (A''), 1976 (A')
<i>mer-2'</i>	-1262.8337334	-1262.5450285	-1262.4692050	0.0758235	2064 (A ₁), 1973 (B ₂), 1947 (A ₁)
<i>fac-2'</i>	-1262.8340414	-1262.5452319	-1262.4689781	0.0762538	2050 (A'), 1978 (A''), 1931 (A')
<i>mer-3'</i>	-1108.0191483	-1107.8011721	-1107.7294282	0.0717439	2072 (A ₁), 1971 (B ₂), 1965 (A ₁)
<i>fac-3'</i>	-1108.0266420	-1107.8089936	-1107.7367397	0.0722539	2061 (A'), 1990 (A''), 1940 (A')

Crystallography

Full details about the collection, solution and refinement are documented in the CIF, which have been deposited with the Cambridge Crystallographic Data Centre under CCDC 1555986 (*mer-1*) and 1555987 (*fac-2*). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting information available

¹H, ¹³C{¹H} and HMBC NMR, and IR spectra of **1** and **2**. Optimised geometries of isomers of **1'**, **2'** and **3'** in Cartesian coordinates.

Acknowledgements

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